

# CHEMICAL COMPOSITION OF DEPLOYED AND INDIGENOUS AQUATIC BRYOPHYTES IN A SEEP FLOWING FROM A PHOSPHATE MINE WASTE PILE AND IN THE ASSOCIATED ANGUS CREEK DRAINAGE, CARIBOU COUNTY, SOUTHEAST IDAHO

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# U. S. DEPARTMENT OF THE INTERIOR U. S. GEOLOGICAL SURVEY

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## **ABSTRACT**

This study reports bulk chemical composition of aquatic bryophyte samples taken from a perennial seep and stream draining the waste pile from a surface phosphate mine in southeastern Idaho. The waste pile has a volume of approximately 4 million m<sup>3</sup> and was completed in 1995. The pile lies in one of two adjacent valleys that form the headwaters of Angus Creek. Sampling occurred at late spring and late summer, 1999, permitting comparison of relatively abundant flow and low-flow conditions, respectively. The study compares a laboratory control sample bryophyte to samples of the same species that were introduced into flowing waters of the seep draining the waste pile and at progressively downstream locations in Angus Creek where they remained submerged for exactly 10 days. The Angus Creek study included placement of a bryophyte sample in an adjacent drainage next to the seeps that was not affected by mining or the waste pile. This serves as a reference site. An additional specimen was deployed 23 km away at a site named Dairy Syncline. It was placed in a stream draining a watershed that contains the same types of phosphatic rocks that are mined and discarded into waste piles but that in this area have not been disturbed by mining. All specimens of introduced bryophytes were Hygrohypnum ochraceum. The study also includes analysis of a single specimen of an indigenous, unidentified bryophyte collected from the seep during the spring sampling.

The data show that concentrations for selected trace elements, relative to the labraised control bryophyte, are elevated by one to two orders of magnitude for the bryophyte sample introduced into the seep and by two to three orders of magnitude for the indigenous sample in the seep water. Selenium has the greatest enrichment. Specimens from the reference and Dairy Syncline sites have Se concentrations that are elevated between a factor of 2 to 4 over the lab-raised control, suggesting that there is a slight regional elevation of the concentrations compared to pristine conditions. After the creek headwaters flow through several beaver ponds and are only 1 km downstream from the seep, the bryophyte trace element concentrations return to levels similar to the control sample, the reference site, and

the Dairy Syncline sample.

# INTRODUCTION

## **Background**

The U.S. Geological Survey (USGS) has studied the Permian Phosphoria Formation in southeastern Idaho and the Western U.S. Phosphate Field throughout much of the twentieth century. In response to a request by the U.S. Bureau of Land Management (BLM), a new series of resource and geoenvironmental studies was initiated by the USGS in 1998. Present studies consist of (1) integrated, multidisciplinary research directed toward resource and reserve estimations of phosphate in selected 7.5-minute quadrangles; (2) elemental residence and mineralogical and petrochemical characteristics; (3) mobilization and reaction pathways, transport, and disposition of potentially toxic elements associated with the occurrence, development, and use of phosphate; (4) geophysical signatures; and (5) improving the understanding of depositional origin. To carry out these studies, the USGS has formed cooperative research relationships with two Federal agencies, the BLM and the U.S. Forest Service (USFS), which are responsible for land management and resource conservation on public lands; and with five private companies currently leasing or developing phosphate resources in southeastern Idaho. The companies are Agrium U.S. Inc. (Rasmussen Ridge mine), Astaris LLC (Dry Valley mine), Rhodia Inc. (Wooley Valley mine-inactive), J.R. Simplot Company (Smoky Canyon mine), and Monsanto Co. (Enoch Valley mine). Because raw data acquired during the project will require time to interpret, the data are released in open-file reports for prompt availability to other workers. The open-file reports associated with this series of resource and geoenvironmental studies are submitted to each of the Federal and industry cooperators for technical review; however, the USGS is solely responsible for the data contained in the reports.

The geoenvironmental aspects of this project consider mobilization and reaction pathways, transport, and disposition of potentially toxic elements associated with the occurrence, development, and mining of phosphate. In particular, the study focuses on the mobilization of selenium and other trace elements from waste rock that is removed from the strip mines during phosphate rock extraction. This waste rock is mined and placed in large piles; either it is backfilled into the mine pit or it is removed from the mine and placed into nearby valleys. In this latter case, drainage percolating through the waste rock pile can leach trace elements from the rock and discharge them into streams draining from the toe of the

waste pile.

This study examines bryophyte samples in a perennial seep and in the creek draining from the Wooley Valley phosphate mine Unit 4 waste pile in southeastern Idaho. The pile lies in one of two adjacent valleys that form the headwaters of Angus Creek. This creek initially flows through Little Long Valley then, after approximately 15 km, into the Blackfoot River. Bryophyte sampling occurred at late spring and late summer, 1999, permitting comparison of relatively abundant- and low-flow conditions, respectively.

The waste pile is approximately 4 million m³ in volume (W. Johnson, BLM, 1999, oral communication; waste dump tonnage is estimated at 6 to 8 megatons at an assumed density of about 1.5 g/cm³) and was completed in 1995. The rocks that comprise the waste pile have been extensively sampled and geochemically characterized at the nearby phosphate mine sites (Herring and others, 1999, 2000a, 2000b, and 2000c). In addition, other components of the ecosystem in and proximal to Little Long Valley have been analyzed, including stream sediments and water from Angus Creek and contentrations of introduced and volatile trace elements (Lamothe and Herring, 2000). All of these various ecosystem components at this locale contain notable enrichments of Se and several other trace elements.

# Sample Locations and Setting

The locations of the sampling stations are shown in figures 1a and 1b. The general area lies approximately 25 km northeast of Soda Springs, Idaho, in an area of southeastern Idaho that has had extensive phosphate mining over the past several decades and currently has four active phosphate mines. Gulbrandsen and Krier (1980) discuss general aspects of the large and rich phosphorus resources in the Phosphoria Formation in the vicinity of Soda Springs, Idaho. Service (1966) provides an evaluation of the western phosphate industry in Idaho and a brief description of the mining history, ore occurrence, and geology. More detailed discussion of the Phosphoria Formation in the Western Phosphate Field is given by McKelvey and others (1959). Unfortunately, most of the analytical descriptions of the phosphatic and associated waste rock units published in these and related works do not include data on several of the important potential contaminant elements. In particular, this includes Se, Cd, and Mo. However, Herring and others (1999, 2000a, and 2000b) list bulk chemical compositional data that includes these elements and several other potential toxicant elements for various lithologies of the phosphatic intervals in the Phosphoria Formation.

Most of the study sites are located in Angus Creek ranging in location from its headwaters to its confluence with the Blackfoot River (figures 1a, 1b). Part of the headwaters are formed by perennial seeps that drain from the toe of the Wooley Valley phosphate mine Unit 4 waste pile. The remaining headwaters emanate from a spring in a valley adjacent to the mine waste pile. After flow through a series of beaver ponds, these headwaters coalesce in a sediment retention reservoir. From the reservoir, the stream flows northwest through Little Long Valley, which has another series of beaver ponds. Angus Creek then flows northeast through a drainage gap in the Wooley Range and then flows southeast into Rasmussen Valley, where cattle graze, on its way to the Blackfoot River. Temperature measurements in the stream during the spring sampling event between sample locations AC4 and AC5 indicate that stream flow below the sediment retention reservoir, site AC4, is approximately tripled by the addition of groundwater (M. Hardy, USGS, oral communication).

The Angus Creek portion of the study included placement of a bryophyte sample in a drainage adjacent to the seeps. This serves as a reference specimen, as the site is not affected by mining or the waste pile. An additional specimen was deployed 23 km away at a site named Dairy Syncline. It was placed in a stream draining a watershed that contains the same types of phosphatic rocks that are mined or from which the waste piles are composed; it is an area that has not yet been disturbed by mining. The study also include analysis of a single specimen of an indigenous bryophyte collected from the seep during the spring sampling.

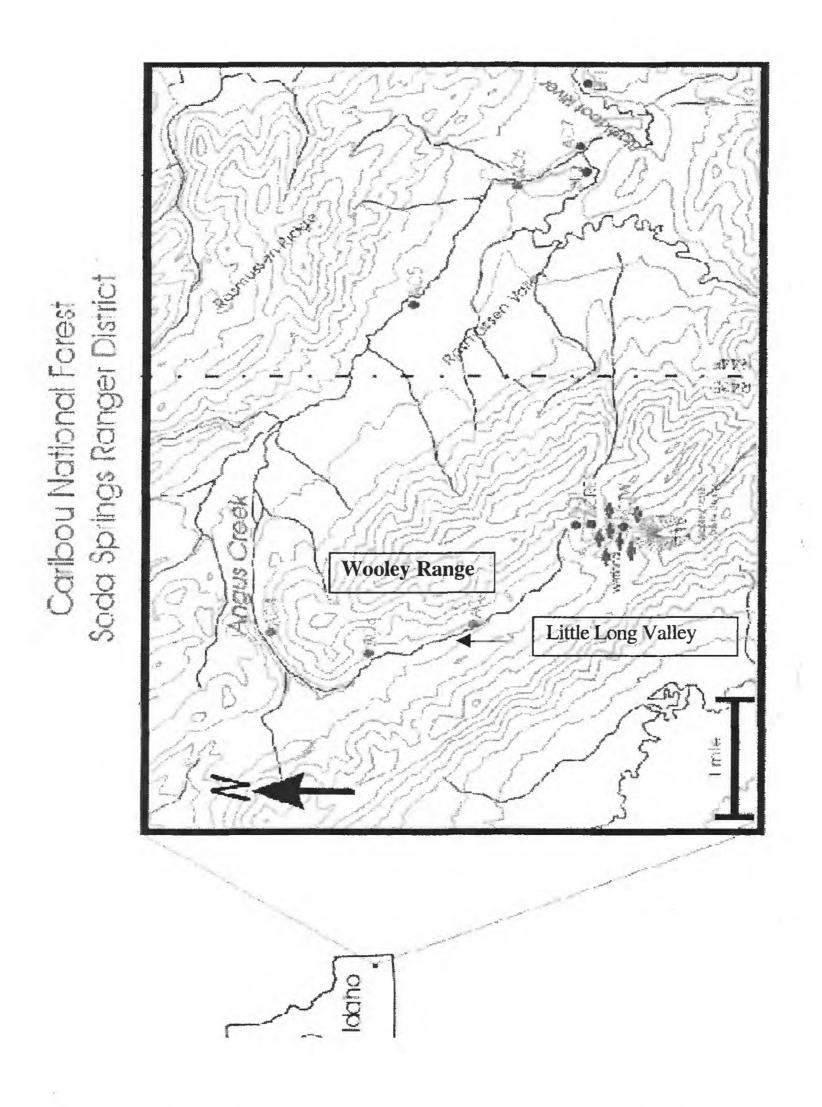


Figure 1a. General location of Angus Creek in southeastern Idaho. Sample sites are shown (AC1...7) and seeps are marked by flying saucer symbols.

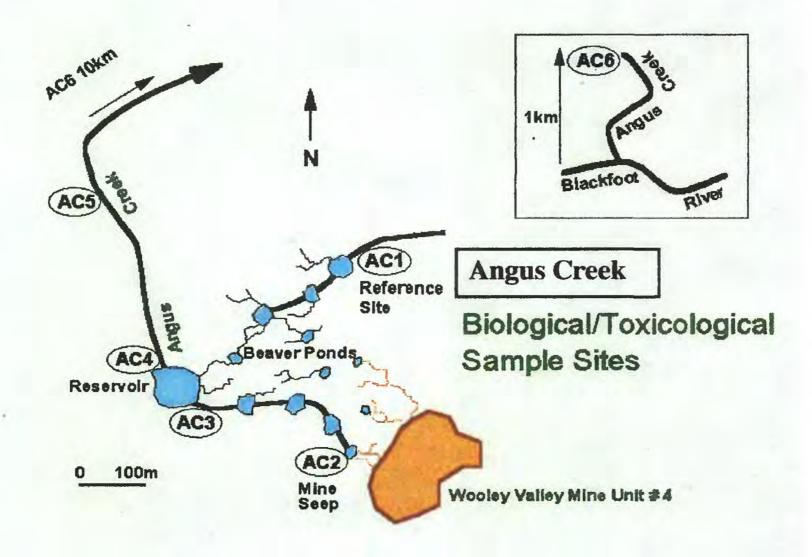


Figure 1b. Diagrammatic depiction of sample sites on Angus Creek showing location of stations used in this study where bryophytes were deployed for 10 days or collected. The reference site, AC1, is a spring that is located about 500 m from the seep and that also drains into Angus Creek. The spring is not affected by the seeps from the mine waste piles. The location for the specimen in the stream at Dairy Syncline is approximately 23 km south-southeast of the seep.

#### **Use of Bryophytes to Monitor Trace Elements**

Aquatic bryophytes—nonvascular plants with differentiated stems and leaves but without true roots—have been used to monitor aquatic concentrations of various trace elements in a variety of settings (see, for example, Bargagli and others, 1987; King and others, 1983; Samecka-Cymerman and Kempers, 1999; Shacklette (1965a and 1965b) and Smith, 1986 and references therein). Generally, the uptake response is thought to mimic the water concentration of the trace elements. However, there are some unknowns in bryophyte uptake response. Notably, these include whether the uptake response is linear and the extent of integration response to a spike or otherwise changing concentrations. The bryophyte specimens used in this study, with the exception of the indigenous specimen, were obtained from a pristine locality in the mountains in Colorado and were harvested by D. Nimmo and C. J. Castle. All specimens of introduced bryophytes were *Hygrohypnum ochraceum*.

#### **METHODS**

# **Field Sampling and Laboratory Controls**

Natural bryophyte samples of approximately 50 g wet weight were placed in net bags and tethered to the stream or seep bottom at the various localities. Specimens were deployed in water for exactly 10 days then recovered. The late spring samples were deployed on 6/16/99, and the late summer samples on 9/15/99. The indigenous sample that was living in the seep at the foot of the mine waste pile was collected into a clean plastic bag and processed like the other samples. When recovered, this specimen was covered with a coating of fine grained, orange material that appeared to be ferrihydrite.

For both the late spring and summer sampling events, a bryophyte specimen was chosen at random and exposed for 10 days to constant-temperature, clean water in laboratory conditions with controlled levels of light and nutrients to simulate healthy, natural growth conditions. This specimen is labeled as the control in the data table and figure.

# **Bryophyte Sample Preparation**

Recovered specimens were placed in a warm drying-oven until dry. The bryophyte samples were disaggregated using a ceramic mortar and pestle and ground to <2 mm. Splits of the material were provided to various analysts for analysis. All splits were obtained with a riffle splitter to ensure similarity with the whole sample.

#### **Analysis**

Samples were analyzed for 40 major, minor, and trace elements using acid digestion in conjunction with inductively-coupled plasma atomic emission spectrometry (ICP-AES). A split was dissolved using a low-temperature (<150°C) digestion with concentrated hydrochloric, hydrofluoric, nitric, and perchloric acids (Arbogast, 1996). The acidic sample solution was taken to dryness and the residue was dissolved with 1 ml of aqua regia and then diluted to 10.0 g with 1% (volume/volume) nitric acid. The concentration analyses are reported on the weight of the sample after ashing at 500°C and can be converted to their respective concentrations in the dry mass of the plant by multiplying by the reciprocal of the ash weight in percent.

Se and As analysis were performed using hydride generation followed by atomic absorption (AA) spectroscopy (Arbogast, 1996). Concentrations are reported based on the dry weight of the plant. For the analysis of Se and As, the hydride analytical technique is considered to be superior to most other analytical techniques. Consequently, the analytical data for As using acid digestion ICP-AES, for which only a single value exceeded the lower detection limit (LDL) of 20 ppm, have been eliminated from the data set and only those for the hydride technique are reported. For all samples, the following elements were reported as being present below their LDL (listed in parentheses in ppm) and were eliminated from the data table: Ag (5), Au (20), As (20), Bi (20), Eu (5), Ho (10), Ta (100), and U (200).

#### RESULTS

Element concentration data for the bryophyte analyses are listed in table 1. There has been no statistical manipulation of the data or consideration of qualified values. Qualified values of concentration result from detection of elements that are present but at concentrations less than their LDL. They are listed in the data table with "<" preceding the LDL.

As a measure of combined analytical, experimental, and laboratory precision, the listings in table 1 include a calculated value of the relative standard difference in percent between the two lab control specimens. The same calculated value is included as a comparison for the two specimens from the reference site locality of Angus Creek.

The abbreviations for analytical techniques in the column headings used in table 1

Hyd.: hydride generation followed by atomic absorption.

ICP-AES: inductively-coupled plasma, atomic emission spectrometry, acid digestion of the residue after ashing.

#### **Observations and Discussion**

are:

Ash weights in the late summer samples are consistently less than those of the late spring samples. This suggests a slight change in growing conditions, such as slightly cooler temperatures or lower light levels.

Essential major elements show only a few spatial or seasonal trends within the creek. Ca in the spring samples decreases downstream along the creek and may be related to the influx of cool ground water that has been noted with Angus Creek. The trend repeats with the late summer samples with the exception of the most downstream sample, just above the confluence with the Blackfoot River. The indigenous bryophyte in the seep appears to have concentrations of K, Mg, Na, and Ti that are a third or less than that of the lab-raised control, which suggests that the conditions in the seep are stressful and restrict healthy growth. However, the increased mass of the sample due to the adsorbed ferrihydrite may cause this apparent reduction. Indeed, if the 32 percent Fe in the ash of the indigenous sample is corrected back to a value of about 4 percent, the effective concentrations of these macronutrient elements will increase to near-similar levels with other samples. The indigenous sample shows the highest concentration of P in the spring samples. Given that the seep is draining phosphatic rocks, this is not surprising. Of the late summer samples, in which an indigenous bryophyte sample was not collected, the seep sample shows the highest P concentration in the Angus Creek system. That level of P decreases with downstream flow, with the exception of the site just above the Blackfoot River where cattle are grazed and may contribute nutrients in their excretions. Spring event samples have higher Ca/P ratios than those of the late summer samples, and suggests greater amounts of Ca in the water relative to P in spring. Alternatively, it could result from the added presence of P in the late summer seep waters after a warm summer and greater dissolution of the phosphatic material in the waste pile.

The indigenous and introduced bryophyte samples at the seep often have the highest concentrations of many of the potential contaminant trace elements. These include Se, Cd, Co, Cr, Cu, Mo, Ni, V, and Zn. Discussion of selected trace elements is included below.

Barium concentrations range from a low of near 700 ppm to a high of 1100 ppm. There is no systematic behavior in the concentration data along the flow of Angus Creek. There is no apparent difference between high- and low-flow times of the year.

Cadmium is highest in the indigenous bryophyte sample, 160 ppm, but this may result from coprecipitation with the ferrihydrite coating. Nonetheless, the introduced bryophyte samples in the seep, which exhibited no visible accumulation of ferrihydrite during their 10-day deployment, have higher concentrations than other samples for both late spring and late summer sampling. The summer sample Cd concentration is triple that of spring and may indicate a change in nature of the flow at the seep.

Like Cd, the highest cobalt concentration occurs in the indigenous sample. This

likely results from association with the ferrihydrite coating.

The seep concentrations of chromium are greater than those of other samples, with the late summer concentration in the introduced sample elevated over that of the spring by roughly the same ratio as Cd. For Cr, the highest concentration does not occur in the spring indigenous seep sample (even though it is elevated about four times that of the introduced seep sample) but in the late summer introduced sample, again suggesting a change in the

chemistry or flow of the seep.

Copper, unlike many of the previous elements, does not have its highest concentration in the introduced or indigenous seep samples for the spring event sampling. In fact, the lowest of the spring concentrations occurs in the indigenous sample. Thus, Cu does not appear to concentrate along with some of the other trace elements in the ferrihydrite coating. However, in the late summer samples the seep specimen at 200 ppm is at least double that of any other concentrations.

Manganese has some concentrations up to nearly 4 percent of the ash weight. This essential minor element also has the highest relative standard difference between the spring and summer event control samples and may reflect some seasonal difference in metabolic

uptake.

Molybdenum is clearly enriched in the seep samples, both indigenous and introduced. Like Cd and Co, the introduced sample in the seep has its higher concentration in the late summer and may suggest changes in conditions at the seep. The Cu/Mo ratio, listed in table 1 and shown in figures 2 and 3, is of particular note. In forage plants consumed by grazers, it is desirable for this ratio to be >2 in order to prevent occurrence of molybdenosis (Erdman, 1990). However, the ration for the indigenous seep sample is much less than this value, 0.13, as is the introduced sample from the late summer sampling, 0.8. The introduced sample from the spring sampling is near to this with a value of 3. It is unknown whether the ratio may be of significance to consumers of aquatic bryophytes. Further, it is unknown whether the low ratio in the indigenous bryophyte results from metabolic uptake or simple sorption to the ferrihydrite coating. Introduced seep samples of the bryophytes did not accumulate a noticeable ferrihydrite coating during deployment. However, low values of the ratio in the samples introduced to the seep strongly suggest that it is the seep water that produces insufficient values of this ratio, at least for bryophytes.

Nickel exhibits the same concentration variability as Mo.

Lead shows no particular enrichment in the seep samples. There does appear to be an approximate doubling of the late summer concentrations over those of the late spring

event sampling.

Selenium in the reference site and Dairy Syncline specimens exhibits concentration enrichments of about a factor of 7 over the laboratory control. This may indicate some slight regional elevation of the Se concentration in the water compared to clean laboratory conditions. Selenium has its highest concentrations in the indigenous and introduced samples from the seep. Concentration enrichments in the introduced specimens are approximately 100-fold over those in the control sample, and in the single indigenous specimen, the enrichment is approximately 1000-fold. However, these concentrations rapidly decrease downstream. After only 1 km of flow along Angus Creek from the seep, the concentrations for spring and fall samples decrease to approximately those of the reference site and Dairy Syncline specimens.

Strontium concentrations appear to be more elevated in the spring event samples. Sr occurs in phosphatic rocks associated with Ca. However, the Sr/Ca and Sr/P ratios do not

show any consistency.

Tin concentrations are generally low, with only a single concentration exceeding

10 ppm.

Vanadium has its highest concentration in the indigenous sample, 1000 ppm. Downstream samples show a progressive decrease in V concentrations, particularly those from the late summer event sampling. Like several other trace elements, the late summer introduced seep sample concentration is greater than that of the spring sample.

Zinc follows a common theme—greatest in the indigenous sample and next highest in the introduced spring and summer seep samples with the late summer event being the greater of the two. Note that the high value is 1 percent Zn in the ash. Zn and Cd

concentrations often behave similarly. Here, the Zn/Cd ratio varies over about a factor of 2, indicating rather similar behavior given the widely varying concentrations of both elements. However, there is some uncertainty in the ratio because of the number of Cd concentrations below the LDL of 4 ppm.

Concentrations of various elements in the bryophyte samples for the two sampling times are graphed in figures 2 and 3. The few "less-than" concentrations reported for some of these elements have been replaced with their lower detection limits for graphing.

#### Summary

In the indigenous bryophyte sample from the seep, several trace elements, notably Cd, Co, Cr, Mo, Ni, V, and Zn, are enriched at levels two to three orders of magnitude over those in the lab-raised control bryophyte. These enrichments in part result from coprecipitation with the iron-rich ferrihydrite coating. Selenium shows the greatest enrichment, approximately 2000-fold. The introduced seep samples do not have noticeable coating accumulation during their deployment time. They also exhibit enrichments of Cd, Cr, Mo, Ni, V, and Zn that likely are related to biological uptake from the seep water. After the creek headwaters flow through several beaver ponds and are only 1 km downstream from the seep, the bryophyte trace element concentrations return to levels similar to the control sample, the reference site sample, and the Dairy Syncline sample. This suggests that trace element concentrations in the stream are progressively diluted and/or rapidly removed by natural processes, such as inclusion into and with the sediments of the beaver ponds. Specimens from the reference and Dairy Syncline sites have Se concentrations that are elevated between a factor of 2 to 4 over the lab-raised control, suggesting that there is a slight regional elevation of the concentrations compared to clean laboratory conditions.

#### ACKNOWLEDGMENTS

The samples from the seep and along Angus Creek were collected from an area operated by the Rhodia Inc. We thank them for providing access. We appreciate help in sample preparation by M. Fallin. We acknowledge technical comments by H. King and the sharp editorial eyes of K. Long. Finally, we appreciate discussion about aquatic bryophytes. their biochemistry, and their response to ambient trace element concentrations in the water with D. Nimmo.

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Angus Creek Bryophytes, Sampled 6/99

10-day deployment, except indigenous; AC1 is reference site; AC2 is Seep; AC3. AC6 are progressively downstream from seep; enrichments shown relative to lab control on log scale (1 = control concentration)

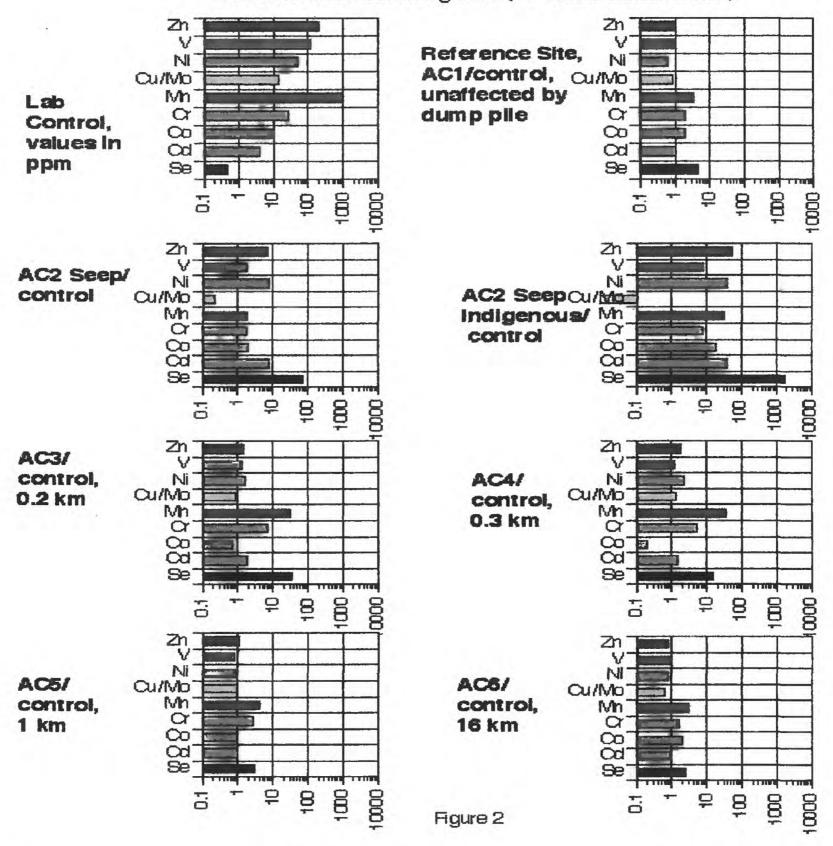


Figure 2. Comparison of selected trace element concentrations in bryophyte samples collected in spring, 1999. The concentration of the selected elements for the lab-raised control bryophyte is shown in the upper left using log-scaled concentration data. All other bryophyte sample concentration data are scaled relative to the control using log-scaled data. A sample with the same concentration of a trace element as the control therefore has a value of one. A sample with 10 times the concentration of the control is shown as 10, and so on. The sample sites progress downstream Angus Creek with approximate distance shown from the seep at the headwaters of Angus Creek. Note the Cu/Mo ratio for the indigenous sample, <0.01.

Angus Creek Bryophytes, Sampled 6/99
10-day deployment, except indigenous; AC1 is reference site; AC2 is Seep;

AC3. AC6 are progressively downstream from seep; enrichments shown relative to lab control on log scale (1 = control concentration)

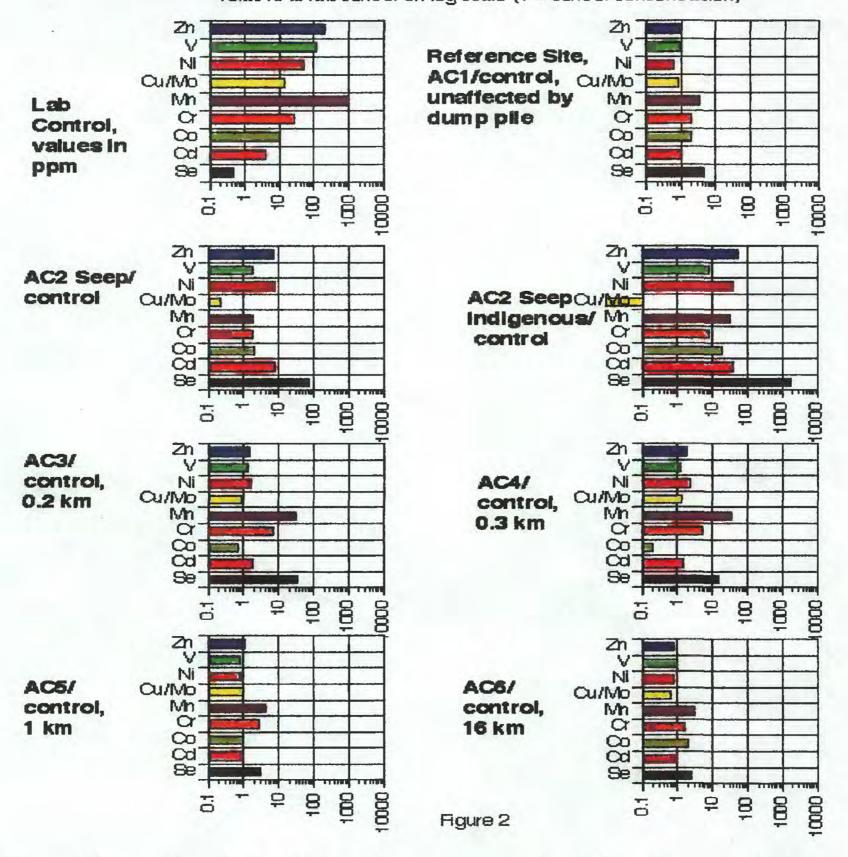


Figure 2. Comparison of selected trace element concentrations in bryophyte samples collected in spring, 1999. The concentration of the selected elements for the lab-raised control bryophyte is shown in the upper left using log-scaled concentration data. All other bryophyte sample concentration data are scaled relative to the control using log-scaled data. A sample with the same concentration of a trace element as the control therefore has a value of one. A sample with 10 times the concentration of the control is shown as 10, and so on. The sample sites progress downstream Angus Creek with approximate distance shown from the seep at the headwaters of Angus Creek. Note the Cu/Mo ratio for the indigenous sample, <0.01.

Angus Creek Bryophytes, Sampled 9/99
10-day deployment; ACI is reference site; AC2 is Seep, AC3. AC6 are progressively downstream from seep; enrichments shown relative to lab control on log scale (1 = control concentration)

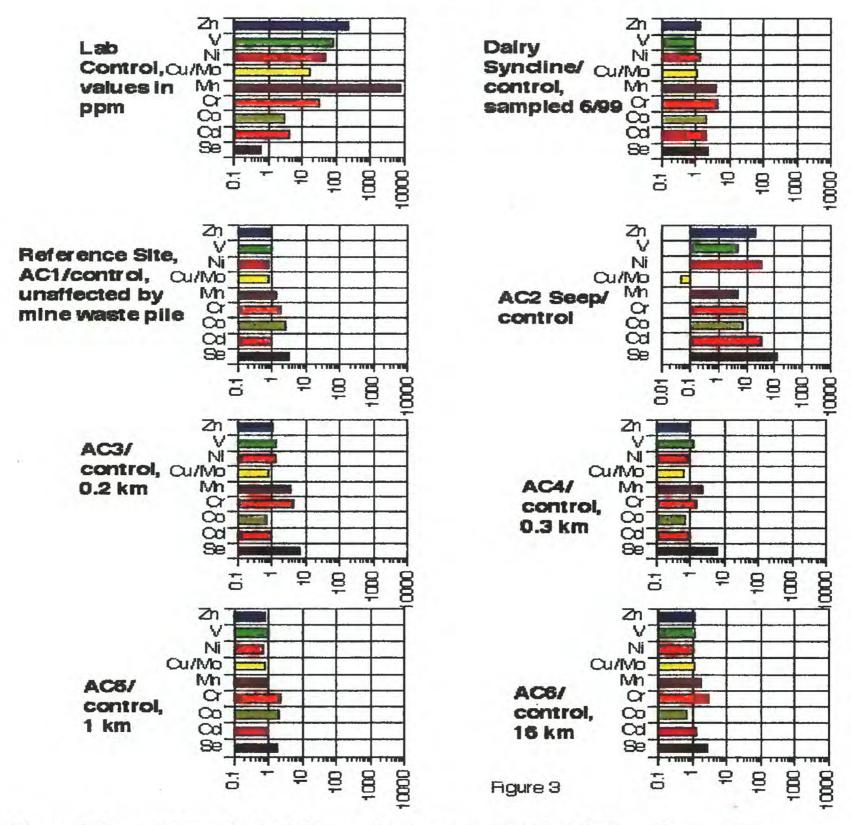


Figure 3. Comparison of selected trace element concentrations in bryophyte samples collected in late summer, 1999, and of the Dairy Syncline sample from spring, 1999. The same comments apply as for figure 2. This sampling event did not include a specimen of the indigenous bryophyte from the seep water. The data from the 6/99 Dairy Syncline sample, which was placed in a stream draining similar phosphatic rocks but ones that are undisturbed by mining, are included on the figure. Note the Cu/Mo ratio for the indigenous sample, <0.1.

Concentrations of major, minor, and trace elements for individual bryophyte samples collected in late spring and late summer, 1999. Table 1.

					+					
Field No.	Locality	Lab Number	Ash, %	As, Hyd., ppm	Se, Hyd., ppm	AI, ICP- AES, %	Ca, ICP- AES, %	Fe, ICP- AES, %	K, ICP- AES, %	Mg, ICP- AES, %
B1	Lab Control	C-138237	52.4	1.1	0.4	8.0	3.5	3.9	2.4	1.4
B2	AC1 (Reference Site)	C-138238	55.3	2.3	2.0	8.0	3.5	4.0	2.6	1.7
B3	Seep-Indigenous	C-138239	64.7	2.9	750	0.5	15	32	6.0	0.5
B4	AC2 (Seep)	C-138240	44.4	3.5	31	7.7	4.8	4.6	2.5	1.5
B5	AC3	C-138241	56.0	5.1	16	6.2	6.1	3.8	1.9	1.3
B6	AC4	C-138242	42.0	2.9	6.4	6.4	6.2	4.1	2.6	1.7
B7	AC5	C-138243	48.5	1.9	1.4	6.9	4.2	3.4	2.5	1.5
B8	AC6	C-138244	65.4	2.3	1:1	7.8	3.6	4.0	2.1	1.3
B9 C	Dairy Syncline	C-138245	54.9	3.6	1.0	7.7	3.4	1.4	2.1	1.3
Fall, 1999 Sar	nples									
8	Lab Control	C-161429	38.1	2.3	9.0	7.4	5.9	3.2	2.0	1.2
AC1	AC1	C-161430	40.9	3.1	1.9	7.2	5.1	3.9	2.2	1.6
AC2	AC2	C-161431	27.7	5.7	80	5.1	10	4.1	2.8	1.6
AC3	AC3	C-161432	34.7	2.9	4.0	6.5	7.0	3.0	2.2	1.5
AC4	AC4	C-161433	38.2	2.7	3.6	7.4	6.4	3.2	1.9	1.6
ACS	AC5	C-161434	45.4	2.8	1.2	7.2	4.8	3.3	2.2	1.4
AC6	AC6	C-161435	35.6	2.6	1.7	6.3	7.5	3.1	2.8	1.5
Relative Stanc	dard Difference: Controls		32%	71%	34%	8%	21%	20%	18%	15%
Relative Stand	Relative Standard Difference: Reference Site	ө	30%	30%	2%	11%	37%	3%	17%	%9

Table 1, continued. Concentrations of major, minor, and trace elements for individual bryophyte samples collected in late spring and late summer, 1999.

Field No.	Locality	Na, ICP- AES, %	P, ICP. AES, %	Ca/P	Ti, ICP. AES, %	Ba, ICP- AES, ppm	Be, ICP- AES, ppm	Cd, ICP-	Ce, ICP- AES, ppm	Co, ICP- AES, ppm
19	Lab Control	1.5	0.4	8.8	0.4	096	<2	4>	83	10
B2	AC1 (Reference Site)	1.3	0.3	10.3	0.4	860	<2	<4	80	20
B3	Seep-Indigenous	0.1	1.1	13.6	0.0	099	<2	160	8>	180
B4	AC2 (Seep)	1.5	0.7	7.4	0.4	950	<2	30	78	20
B5	AC3	1.0	9.0	10.2	0.3	840	<2	7	70	7
B6	AC4	1.0	0.8	7.8	0.3	1100	<2	9	20	<2
87	AC5	1.1	4.0	10.0	0.3	720	<2	<4	76	10
B8	AC6	1.4	0.3	12.0	0.4	930	<2	<4	85	20
89	Dairy Syncline	F.	0.4	8.5	0.4	920	<2	Φ	78	21
Fall, 1999 Samples	les									
8	Lab Control	1.2	9.0	9.5	0.3	1100	3	<b>4</b> >	84	က
AC1	AC1	0.7	9.0	9.1	0.3	670	က	<b>^</b>	86	Φ
AC2	AC2	9.0	1.7	5.9	0.2	690	2	130	59	22
AC3	AC3	0.8	6.0	8.1	0.2	720	2	4	70	<2
AC4	AC4	1.1	0.7	9.7	0.3	830	3	<b>4</b> >	82	<2
ACS	AC5	6.0	0.5	9.6	0.3	620	က	44	86	9
AC6	AC6	0.7	1:	6.8	0.3	096	2	D.	69	<2
Relative Standar	Relative Standard Difference: Controls	22%	46%		33%	14%			1%	108%
Relative Standar	Relative Standard Difference: Reference Site	65%	46%		42%	25%			7%	86%

Table 1, continued. Concentrations of major, minor, and trace elements for individual bryophyte samples collected in late spring and late summer, 1999.

Field No.	Locality	Cr, ICP-	Cu, ICP-	Ga, ICP-	La, ICP-	Li, ICP-	Mn, ICP-	Mo, ICP-	Cu/Mo	Nb, ICP-
B1	Lab Control	27	56	20	45	23	1000	4	>14	20
B2	AC1 (Reference Site)	50	46	20	43	36	3400	4 >	>12	6
B3	Seep-Indigenous	210	20	8 >	10	2	33000	160	0.13	×8
B4	AC2 (Seep)	47	62	10	42	20	1800	20	3.1	20
B5	AC3	190	48	31	44	27	30000	4	12	8
B6	AC4	140	75	24	42	26	36000	v 22	>15	<10
B7	AC5	71	55	20	41	34	4300	4	14	×8
B8	AC6	44	34	20	46	26	3200	4>	>8.5	10
B9	Dairy Syncline	120	59	20	41	33	3900	4	715	6
Fall 1999 Samples	Selo									
8	Lab Control	30	69	20	42	32	7400	<b>*</b>	>17	8 >
AC1	AC1	55	51	20	44	42	10000	4 >	>13	8>
AC2	AC2	300	200	<8>	42	25	35000	250	0.8	<8
AC3	AC3	130	63	20	40	31	27000	5	13	× × 8
AC4	AC4	42	41	20	43	32	17000	4	10	8 >
AC5	AC5	68	51	20	44	40	7400	4 >	>13	8>
AC6	AC6	91	80	20	39	39	13000	× ×	>20	8>
Relative Standar	Relative Standard Difference: Controls	11%	21%	%0	7%	33%	152%			
Relative Standa	Relative Standard Difference: Reference Site	10%	10%	%0	2%	15%	%66			

Table 1, continued. Concentrations of major, minor, and trace elements for individual bryophyte samples collected in late spring and late summer, 1999.

Field No.	Locality	Nd, ICP- AES, ppm	Ni, ICP- AES, ppm	Pb, ICP. AES, ppm	Sc, ICP- AES, ppm	Sn, ICP- AES, ppm	Sr, ICP- AES, ppm	Sr/Ca	Sr/P	Th, ICP- AES, ppm
B1	Lab Control	34	53	20	10	10	620	177	1550	10
B2	AC1 (Reference Site)	31	32	20	10	10	460	131	1353	10
B3	Seep-Indigenous	<8	2000	×8×	80	<10	410	27	373	8 >
B4	AC2 (Seep)	32	420	80	10	10	650	135	1000	10
B5	AC3	<8>	85	10	10	<10	460	75	767	10
B6	AC4	<10	120.	10	10	20	520	84	650	10
B7	AC5	32	44	10	10	<10	400	98	952	10
B8	AC6	35	41	6	10	<10	580	161	1933	10
B9	Dairy Syncline	30	69	20	10	<10	440	129	1100	10
Fall, 1999 Samples	ples		1							
88	Lab Control	27	50	42	6	<10	270	46	422	10
AC1	AC1	27	37	34	10	<10	210	41	375	10
AC2	AC2	<8	1600	20	7	<10	350	35	206	50
AC3	AC3	<8	69	26	8	<10	350	20	407	10
AC4	AC4	20	44	30	6	<10	350	55	530	10
AC5	AC5	32	37	30	10	<10	240	20	480	10
AC6	AC6	21	53	26	10	<10	300	40	273	10
Relative Stands	Relative Standard Difference: Controls	23%	%9	71%	11%		%62	118%		%0
Relative Stands	Relative Standard Difference: Reference Site		-	52%	%0		75%			%0

1, continued. Concentrations of major, minor, and trace elements for individual bryophyte samples collected in late spring and late summer, 1999. Table

Field No.	Locality	V, ICP- AES, ppm	Y, ICP- AES, ppm	Yb, ICP- AES, ppm	Zn, ICP- AES, ppm	Zn/Cd
B1	Lab Control	120	20	<2	200	>50
B2	AC1 (Reference Site)	110	23	2	200	>50
B3	Seep-Indigenous	1000	21	2	11000	69
B4	AC2 (Seep)	220	20	<2	1400	47
B5	AC3	150	28	3	280	40
B6	AC4	140	25	2	370	62
B7	AC5	98	25	2	210	>52.5
B8	AC6	110	24	2	150	>37.5
B9	Dairy Syncline	120	26	2	270	34
Fall, 1999 Samples	les					
	Lab Control	86	20	<2	220	>55
AC1	AC1	82	26	2	180	>45
AC2	AC2	420	30	2	4700	36
AC3	AC3	110	23	2	240	09
AC4	AC4	100	20	2	210	>52.5
AC5	ACS	82	27	2	170	>42.5
AC6	AC6	98	27	က	260	52
Relative Standard Difference:	d Difference: Controls	33%	%0		10%	
Relative Standard Difference:	d Difference: Reference Site	29%	12%	%0	11%	